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* * * * * STN Columbus * * * * *

FILE 'HOME' ENTERED AT 06:00:37 ON 28 OCT 2005

=> file reg

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
0.21	0.21

FULL ESTIMATED COST

FILE 'REGISTRY' ENTERED AT 06:00:48 ON 28 OCT 2005
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STRUCTURE FILE UPDATES: 26 OCT 2005 HIGHEST RN 866186-08-5
DICTIONARY FILE UPDATES: 26 OCT 2005 HIGHEST RN 866186-08-5

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*

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<http://www.cas.org/ONLINE/UG/regprops.html>

=> e 2,4,6,8-Nonatetraenoic acid, 2-cyano-9-phenyl-/cn

E1	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FUR	ETHYL E
		L ESTER/CN	
E2	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-ALL-E)-/CN	ETHYL E
		STER/CN	
E3	1	--> 2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-	ETHYL E
E4	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYAN	ETHYL E
E5	1	2,4,6,8-NONATETRAENOIC ACID, 2-CY	ETHYL E
		CN	
E6	1	2,4,6,8-NONATETRAENOIC ACID,	

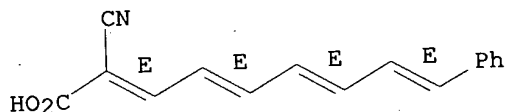
E7 1 CN
 2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, METHYL ESTER
 /CN
 E8 1 2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI
 METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (ALL-E)-/CN
 E9 1 2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI
 METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (Z,E,E,E)-/CN
 E10 1 2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI
 METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (Z,E,E,Z)-/CN
 E11 1 2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,5-DIMET
 HYL-1,3-CYCLOHEXADIEN-1-YL)-3,7-DIMETHYL-, ETHYL ESTER, (ALL
 -E)-/CN
 E12 1 2,4,6,8-NONATETRAENOIC ACID, 2-METHOXY-9-PHENYL-, ETHYL ESTE
 R/CN

=> e4
 L1 1 "2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, (ALL-E)-"/CN

=> d 11

L1 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
 RN 81620-82-8 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN **2,4,6,8-Nonatetraenoic acid, 2-cyano-9-phenyl-, (all-E)- (9CI)**
 (CA INDEX NAME)
 FS STEREOSEARCH
 MF C16 H13 N O2
 LC STN Files: BEILSTEIN*, CA, CAPLUS, CASREACT
 (*File contains numerically searchable property data)

Double bond geometry as shown.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus
 COST IN U.S. DOLLARS
 FULL ESTIMATED COST

SINCE FILE	TOTAL
ENTRY	SESSION
6.87	7.08

FILE 'CAPLUS' ENTERED AT 06:01:30 ON 28 OCT 2005
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FILE LAST UPDATED: 26 Oct 2005 (20051026/ED)

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=> l1

L2 1 L1

=> d l2 ti fbib abs

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2005 ACS on STN
TI Structural effect in cross conjugative systems. IV. Properties of
 α -carboxyphenylpolyenic cyanides and the quantum chemical
calculation of orbital energy and bond order
AN 1982:180289 CAPLUS
DN 96:180289
TI Structural effect in cross conjugative systems. IV. Properties of
 α -carboxyphenylpolyenic cyanides and the quantum chemical
calculation of orbital energy and bond order
AU Liang, Desheng; Lai, Chugen; Chiang, Mingchien
CS Inst. Chem., Acad. Sin., Shanghai, Peop. Rep. China
SO Fenzi Kexue Xuebao (1981-1982) (1981), 1(1), 17-30
CODEN: FKXUDX; ISSN: 0253-3677
DT Journal
LA Chinese
AB all-trans-Ph(CH:CH)nCH:C(CN)CO₂H (I) are prepared and their UV and mass
spectra are observed. The MO, π -energy differences, and π -bond orders
of I are calculated by CNDO/2. The properties of I are correctly calculated by
using the extended form of the homologous equation for the corresponding
linear conjugated system (ω -phenylpolyenic nitriles) with an
 α -CO₂H group substituent. Cross-conjugated systems may be generally
treated by allowing 1 of the 2 branches to become the terminal group of a
linear conjugated system while the other branch becomes the substituent.

=> file reg

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
3.55	10.63

FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE	TOTAL
ENTRY	SESSION
-0.73	-0.73

CA SUBSCRIBER PRICE

FILE 'REGISTRY' ENTERED AT 06:02:34 ON 28 OCT 2005
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DICTIONARY FILE UPDATES: 26 OCT 2005 HIGHEST RN 866186-08-5

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*
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added,   *
* effective March 20, 2005. A new display format, IDERL, is now     *
* available and contains the CA role and document type information. *
*
*****
```

Structure search iteration limits have been increased. See HELP SLIMITS
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REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document. For information
on property searching in REGISTRY, refer to:

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=> e3

L3 1 "2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-"/CN

=> d 13

L3 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2005 ACS on STN
RN 412036-67-0 REGISTRY
ED Entered STN: 07 May 2002
CN 2,4,6,8-Nonatetraenoic acid, 2-cyano-9-phenyl- (9CI) (CA INDEX
NAME)
FS 3D CONCORD
MF C16 H13 N O2
SR Reaction Database
LC STN,Files: CA, CAPLUS, CASREACT



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	6.87	17.50
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL

CA SUBSCRIBER PRICE

ENTRY	SESSION
0.00	-0.73

FILE 'CAPLUS' ENTERED AT 06:02:57 ON 28 OCT 2005
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=> L3

L4 1 L3

=> d L4

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2005 ACS on STN
AN 1939:54119 CAPLUS
DN 33:54119
OREF 33:7758d-i,7759a-i,7760a
TI Preparation of polyunsaturated nitriles and aldehydes. II
AU Wittig, Georg; Hartmann, Helmut
SO Ber. (1939), 72B, 1387-98
DT Journal
LA Unavailable
OS CASREACT 33:54119

=> file reg

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
3.35	20.85

FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE	TOTAL
ENTRY	SESSION
0.00	-0.73

CA SUBSCRIBER PRICE

FILE 'REGISTRY' ENTERED AT 06:06:09 ON 28 OCT 2005
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STRUCTURE FILE UPDATES: 26 OCT 2005 HIGHEST RN 866186-08-5

DICTIONARY FILE UPDATES: 26 OCT 2005 HIGHEST RN 866186-08-5

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*
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* available and contains the CA role and document type information. *
*
*****
```

Structure search iteration limits have been increased. See HELP SLIMITS
for details.

REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document. For information
on property searching in REGISTRY, refer to:

<http://www.cas.org/ONLINE/UG/regprops.html>

=> e e1

E1	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYL)-, ETHYL E STER/CN
E2	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYLOXY)-/CN
E3	1 -->	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYLOXY)-, ETHY L ESTER/CN
E4	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-THIENYL)-, ETHYL E STER/CN
E5	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-/CN
E6	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, (ALL-E)-/CN
E7	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, BUTYL ESTER/ CN
E8	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, ETHYL ESTER/ CN
E9	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, METHYL ESTER /CN
E10	1	2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (ALL-E)-/CN
E11	1	2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (Z,E,E,E)-/CN
E12	1	2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (Z,E,E,Z)-/CN

=> e e1

E1	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-3,7-DIMETHYL-9-(2,6,6-T RIMETHYL-1-CYCLOHEXEN-1-YL)-, ETHYL ESTER/CN
E2	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-((2,2-DICYANO-1-PHENY LVINYLA)MINO)-3-ETHYL-, METHYL ESTER/CN
E3	1 -->	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYL)-, ETHYL E STER/CN
E4	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYLOXY)-/CN
E5	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-FURANYLOXY)-, ETHY L ESTER/CN
E6	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-(2-THIENYL)-, ETHYL E

		STER/CN
E7	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-/CN
E8	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, (ALL-E)-/CN
E9	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, BUTYL ESTER/ CN
E10	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, ETHYL ESTER/ CN
E11	1	2,4,6,8-NONATETRAENOIC ACID, 2-CYANO-9-PHENYL-, METHYL ESTER /CN
E12	1	2,4,6,8-NONATETRAENOIC ACID, 2-FLUORO-9-(4-METHOXY-2,3,6-TRI METHYLPHENYL)-3,7-DIMETHYL-, ETHYL ESTER, (ALL-E)-/CN

=> d l4 ti fbib abs

YOU HAVE REQUESTED DATA FROM FILE 'CAPLUS' - CONTINUE? (Y)/N:n

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	1.29	22.14
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	0.00	-0.73

FILE 'CAPLUS' ENTERED AT 06:07:47 ON 28 OCT 2005

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=> d l4 ti fbib abs

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2005 ACS on STN
 TI Preparation of polyunsaturated nitriles and aldehydes. II
 AN 1939:54119 CAPLUS
 DN 33:54119
 OREF 33:7758d-i,7759a-i,7760a
 TI Preparation of polyunsaturated nitriles and aldehydes. II
 AU Wittig, Georg; Hartmann, Helmut
 SO Ber. (1939), 72B, 1387-98
 DT Journal
 LA Unavailable
 OS CASREACT 33:54119

AB cf. C. A. 30, 8201.2. In part I was described a process for the stepwise preparation of vinylene-homologous aldehydes: $\text{RCHO} + \text{CH}_2(\text{CN})\text{CO}_2\text{H} \rightarrow \text{RCH}:\text{C}(\text{CN})\text{CO}_2\text{H} \rightarrow \text{RCH}:\text{CHCN} \rightarrow \text{RCH}:\text{CHCH}:\text{NH} \rightarrow \text{RCH}:\text{CHCHO}$. The applicability of this method is limited, however, by the increasing difficulty with which the unsatd. nitriles are reduced by SnCl_2 in $\text{HCl-Et}_2\text{O}$ with increasing length of the conjugated system. To obtain further information on the reaction, addnl. nitriles have been prepared under various condensation conditions and the possibility of their reduction with SnCl_2 and other metal halides studied. Of special interest was the condensation of aldehydes with $\text{Me}_2\text{C}:\text{C}(\text{CN})\text{CO}_2\text{Me}$ (I), for decarboxylation and reduction of the products offered the possibility of building up "isoprene" chains. Model expts. were first carried out with BzH and $\text{PhCH}:\text{CHCHO}$. Whereas in boiling glacial AcOH alone or in the presence of AcNH_2 or AcNEt_2 reaction was very slow, addition of AcONH_4 resulted within 20 min. in a reaction which, however, followed a different course from that desired; BzH gave in good yield $\text{PhCH}:\text{C}(\text{CN})\text{CO}_2\text{Me}$, m. $88-9^\circ$ (16 g. from 10.6 g. BzH, 13.9 g. I and 0.5 g. AcONH_4 in 10 cc. AcOH at 120°). Apparently I decompose in the presence of AcONH_4 into Me_2CO and $\text{CH}_2(\text{CN})\text{CO}_2\text{Me}$ and the resulting equilibrium is continuously disturbed by removal of the $\text{CH}_2(\text{CN})\text{CO}_2\text{Me}$ by condensation with the BzH. Similarly, with $\text{PhCH}:\text{CHCHO}$ was obtained $\text{PhCH}:\text{CHCH}:\text{C}(\text{CN})\text{CO}_2\text{Me}$, m. $143.4-4.5^\circ$. The condensation with BzH proceeded as desired, however, by working at 45° and using 10 drops piperidine (II) and 0.4 g. II.AcOH as the condensing agent. After 3 h., drops of water had separated which were removed in vacuo; as the II also distilled over, 10 drops was again added and the distillation and addition of fresh II were repeated until no further separation of water occurred and the odor of BzH had disappeared (about 2 days). The resulting red lake, taken up in 20 cc. hot MeOH, yielded Me 2-cyano-3-methyl-5-phenyl-2,4-pentadienoate, $\text{PhCH}:\text{CHCMe}:\text{C}(\text{CN})\text{CO}_2\text{Me}$, m. $110.5-11.5^\circ$; a further amount was obtained from the mother liquors (total yield, 85%). The nitrilocarboxylic ester group in I, like the carbonyl group in $\text{MeCH}:\text{CHCHO}$, makes the end Me group capable of condensing, although the latter is separated from the activating group by a C:C union, probably because the polar CN group polarizes the C:C union ($+\text{H} \cdot -\text{C} \cdot +\text{C} \cdot -\text{C} \cdot +\text{C} \cdot \text{tpbond} \cdot -\text{N}$) which, in turn, by polarization increases in the Me group the tendency to give off protons; this loosening of the C.H union is a prerequisite of addition to the aldehyde group. When the CN group in I is replaced by CO_2Et or $\text{CONHC}_6\text{H}_4\text{Me}$, condensation takes place with neither BzH nor $\text{PhCH}:\text{CHCHO}$ under the above conditions; the effect of these polar groups extends only to an adjacent group (as in $\text{CH}_2(\text{CO}_2\text{Et})_2$ or its toluidide). That, on the other hand, the influence of a CN group extends through even a conjugated system of 2 C:C unions is shown by the condensation of $\text{MeCH}:\text{CHCH}:\text{C}(\text{CN})\text{CO}_2\text{Me}$ by means of II-II.AcOH with $\text{PhCH}:\text{CHCHO}$ to give Me 2-cyano-9-phenyl-2,4,6,8-nonatetraenoate (III) (25%), bright red, m. $168-9^\circ$. The addition of an "isopentane" to aldehydes thus made possible by condensation with I can also be effected by condensation first with acetone and then with $\text{CH}_2(\text{CN})\text{CO}_2\text{Me}$. This method is of practical importance in the case of β -ionone, itself a condensation product with acetone; 19.2 g. with $\text{CH}_2(\text{CN})\text{CO}_2\text{Me}$ and AcNH_2 - AcONH_4 in boiling AcOH gives 21 g. Me 2-cyano- β -ionylideneacetate, b0.38 $171-2^\circ$ (with AcNH_2 alone there is no appreciable reaction). The ester (20 g.), shaken with 140 cc. N NaOH at 90° until a homogeneous solution is formed and acidified with dilute HCl, gives 19 g. of the free acid, which, heated with Naturkupper C at 150° , yields 11.5 g. β -ionylideneacetonitrile, b1 $117-22^\circ$, also obtained directly in 13 g. yield from 19.2 g. β -ionone with $\text{CH}_2(\text{CN})\text{CO}_2\text{H}$, AcNH_2 and AcONH_4 in boiling AcOH. Before reduction of the above cyano esters the CO_2Me group had to be removed. This was effected by saponification to the cyano acid with dilute NaOH or, if resinification occurred, with $\text{Ba}(\text{OH})_2$ in MeOH, and decarboxylation by heating and distilling over Cu powder. Thus, III gave nearly quant. the free

cyano acid, deep red, m. 219-22° which yielded 70% of a mixture of stereoisomeric 9-phenyl-2,4,6,8-nonatetraene-1-nitriles, b0.025 160-75° as a yellowish oil solidifying on rubbing with MeOH to crystals whose m. p. was raised by repeated crystallization from MeOH from 80° to 149° but this high-melting fraction amounted to only 10% of the original product; the MeOH mother liquors with water gave a viscous yellow oil of the same composition As model substances for the

reduction

of the unsatd. nitriles were taken PhCN, PhCH:CHCN and Ph(CH:CH)2CN. As shown in part I, with SnCl2 in HCl-ether these nitriles give about 90, 40 and 10%, resp., of the corresponding aldimides or aldehydes. In an effort to overcome this rapid decrease in yield with increasing length of the chain, stronger reducing agents were investigated. Neither PhCN nor PhCH:CHCN could be reduced with CrCl2 in HCl-ether or HCl-dioxane up to 80°, with CrBr2 in HBr-ether or with VCl2 or TiCl3 in HCl-ether.

formation

Anhydrous SnBr2 dissolved in absolute ether in a few min. without layer when HBr was passed in, and when the nitriles were added to the solution the crystalline imide bromides separated at first but soon disappeared again with formation of 2 liquid layers; after 3 days' shaking the yellow crystals of the HBr-SnBr4 addition products which had separated yielded 73, 65 and 50%, resp., of the aldehydes corresponding to the above 3 nitriles. Similarly, Ph2C:CHCH:CHCN gave 46% Ph2C:CHCH:CHCHO, whereas with SnCl2 the yield was only 10%. With pure dioxane instead of absolute ether the reduction can be effected at 55-60°; the reduction mixture remains homogeneous, and although the yields are 2-4% lower the reduction time is decreased to 20 min. The effectiveness of SnBr2-HBr is also limited, however, in that it does not convert 3-fold (or more) unsatd. nitriles into the aldimides. Thus, Ph(CH:CH)3CN (IV) is in large part recovered unchanged. The explanation suggested in part I for the decreased yields with polyunsatd. nitriles, viz., that the SnCl2-HCl addition products become increasingly more difficultly soluble, does not hold, since IV forms with SnBr2 in HBr-ether a homogeneous solution which even after days yields no reduction product. The vinylene homologs of PhCN form with HCl or HBr in ether imide halides whose color deepens with increasing number of C:C unions and which become increasingly difficultly soluble in ether, a phenomenon which is to be explained by increasing polarity of the C-halogen union. The reduction would then proceed according to the scheme $[RC^+:NH][HSnCl_4]^- (V) \rightarrow RCH:NH + SnCl_4$. In 3-fold unsatd. imide halides the halogen acid is split off from the Sn salt because the CN group conjugated with 3 C:C unions cannot hold the halogen acid firmly enough, and reduction, for which formation of the complex V is a prerequisite, cannot occur. A specially constructed apparatus, which made it possible to carry out simultaneously comparative redns. of several nitriles under identical conditions at different temps., is described.

=>

Connection closed by remote host

---Logging off of STN---

END

Unable to generate the STN prompt.
Exiting the script...

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2005 ACS on STN
TI Preparation of polyunsaturated nitriles and aldehydes. II
AN 1939:54119 CAPLUS
DN 33:54119

OREF 33:7758d-i,7759a-i,7760a

TI Preparation of polyunsaturated nitriles and aldehydes. II

AU Wittig, Georg; Hartmann, Helmut

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AB cf. C. A. 30, 8201.2. In part I was described a process for the stepwise preparation of vinylene-homologous aldehydes: $RCHO + CH_2(CN)CO_2H \rightarrow RCH:C(CN)CO_2H \rightarrow RCH:CHCN \rightarrow RCH:CHCH:NH \rightarrow RCH:CHCHO$.

The applicability of this method is limited, however, by the increasing difficulty with which the unsatd. nitriles are reduced by $SnCl_2$ in $HCl-Et_2O$ with increasing length of the conjugated system. To obtain further information on the reaction, addnl. nitriles have been prepared under various condensation conditions and the possibility of their reduction with $SnCl_2$ and other metal halides studied. Of special interest was the condensation of aldehydes with $Me_2C:C(CN)CO_2Me$ (I), for decarboxylation and reduction of the products offered the possibility of building up "isoprene" chains. Model expts. were first carried out with BzH and $PhCH:CHCHO$. Whereas in boiling glacial $AcOH$ alone or in the presence of $AcNH_2$ or $AcNEt_2$ reaction was very slow, addition of $AcONH_4$ resulted within 20 min. in a reaction which, however, followed a different course from that desired; BzH gave in good yield $PhCH:C(CN)CO_2Me$, m. $88-9^\circ$ (16 g. from 10.6 g. BzH , 13.9 g. I and 0.5 g. $AcONH_4$ in 10 cc. $AcOH$ at 120°). Apparently I decompose in the presence of $AcONH_4$ into Me_2CO and $CH_2(CN)CO_2Me$ and the resulting equilibrium is continuously disturbed by removal of the $CH_2(CN)CO_2Me$ by condensation with the BzH . Similarly, with $PhCH:CHCHO$ was obtained $PhCH:CHCH:C(CN)CO_2Me$, m. $143.4-4.5^\circ$. The condensation with BzH proceeded as desired, however, by working at 45° and using 10 drops piperidine (II) and 0.4 g. II. $AcOH$ as the condensing agent. After 3 h., drops of water had separated which were removed in vacuo; as the II also distilled over, 10 drops was again added and the distillation and addition of fresh II were repeated until no further separation of water

occurred and the odor of BzH had disappeared (about 2 days). The resulting red lake, taken up in 20 cc. hot $MeOH$, yielded Me 2-cyano-3-methyl-5-phenyl-2,4-pentadienoate, $PhCH:CHCMe:C(CN)CO_2Me$, m. $110.5-11.5^\circ$; a further amount was obtained from the mother liquors (total yield, 85%). The nitrilocarboxylic ester group in I, like the carbonyl group in $MeCH:CHCHO$, makes the end Me group capable of condensing, although the latter is separated from the activating group by a C:C union, probably because the polar CN group polarizes the C:C union ($+H.-C.+C.-C.+C.tplbond.-N$) which, in turn, by polarization increases in the Me group the tendency to give off protons; this loosening of the C.H union is a prerequisite of addition to the aldehyde group. When the CN group in I is replaced by CO_2Et or $CONHC_6H_4Me$, condensation takes place with neither BzH nor $PhCH:CHCHO$ under the above conditions; the effect of these polar groups extends only to an adjacent group (as in $CH_2(CO_2Et)_2$ or its toluidide). That, on the other hand, the influence of a CN group extends through even a conjugated system of 2 C:C unions is shown by the condensation of $MeCH:CHCH:C(CN)CO_2Me$ by means of II-II. $AcOH$ with $PhCH:CHCHO$ to give Me 2-cyano-9-phenyl-2,4,6,8-nonatetraenoate (III) (25%), bright red, m. $168-9^\circ$. The addition of an "isopentane" to aldehydes thus made possible by condensation with I can also be effected by condensation first with acetone and then with $CH_2(CN)CO_2Me$. This method is of practical importance in the case of β -ionone, itself a condensation product with acetone; 19.2 g. with $CH_2(CN)CO_2Me$ and $AcNH_2-AcONH_4$ in boiling $AcOH$ gives 21 g. Me 2-cyano- β -ionylideneacetate, b_{0.38} $171-2^\circ$ (with $AcNH_2$ alone there is no appreciable reaction). The ester (20 g.), shaken with 140 cc. N $NaOH$ at

90° until a homogeneous solution is formed and acidified with dilute HCl, gives 19 g. of the free acid, which, heated with Naturkupfer C at 150°, yields 11.5 g. β -ionylideneacetonitrile, b1

117-22°, also obtained directly in 13 g. yield from 19.2 g.

β -ionone with $\text{CH}_2(\text{CN})\text{CO}_2\text{H}$, AcNH_2 and AcONH_4 in boiling AcOH . Before reduction of the above cyano esters the CO_2Me group had to be removed. This was effected by saponification to the cyano acid with dilute NaOH or, if resinification occurred, with $\text{Ba}(\text{OH})_2$ in MeOH , and decarboxylation by heating and distilling over Cu powder. Thus, III gave nearly quant. the free cyano acid, deep red, m. 219-22° which yielded 70% of a mixture of stereoisomeric 9-phenyl-2,4,6,8-nonatetraene-1-nitriles, b0.025 160-75° as a yellowish oil solidifying on rubbing with MeOH to crystals whose m. p. was raised by repeated crystallization from MeOH from 80° to 149° but this high-melting fraction amounted to only 10% of the original product; the MeOH mother liquors with water gave a viscous yellow oil of the same composition As model substances for the

reduction

of the unsatd. nitriles were taken PhCN , PhCH:CHCN and $\text{Ph}(\text{CH:CH})_2\text{CN}$. As shown in part I, with SnCl_2 in HCl -ether these nitriles give about 90, 40 and 10%, resp., of the corresponding aldimides or aldehydes. In an effort to overcome this rapid decrease in yield with increasing length of the chain, stronger reducing agents were investigated. Neither PhCN nor PhCH:CHCN could be reduced with CrCl_2 in HCl -ether or HCl -dioxane up to 80°, with CrBr_2 in HBr -ether or with VCl_2 or TiCl_3 in HCl -ether.

Anhydrous SnBr_2 dissolved in absolute ether in a few min. without layer

formation

when HBr was passed in, and when the nitriles were added to the solution the crystalline imide bromides separated at first but soon disappeared again with formation of 2 liquid layers; after 3 days' shaking the yellow crystals of the HBr-SnBr_4 addition products which had separated yielded 73, 65 and 50%, resp., of the aldehydes corresponding to the above 3 nitriles. Similarly, $\text{Ph}_2\text{C:CHCH:CHCN}$ gave 46% $\text{Ph}_2\text{C:CHCH:CHCHO}$, whereas with SnCl_2 the yield was only 10%. With pure dioxane instead of absolute ether the reduction can be effected at 55-60°; the reduction mixture remains homogeneous, and although the yields are 2-4% lower the reduction time is decreased to 20 min. The effectiveness of $\text{SnBr}_2\text{-HBr}$ is also limited, however, in that it does not convert 3-fold (or more) unsatd. nitriles into the aldimides. Thus, $\text{Ph}(\text{CH:CH})_3\text{CN}$ (IV) is in large part recovered unchanged. The explanation suggested in part I for the decreased yields with polyunsatd. nitriles, viz., that the $\text{SnCl}_2\text{-HCl}$ addition products become increasingly more difficultly soluble, does not hold, since IV forms with SnBr_2 in HBr -ether a homogeneous solution which even after days yields no reduction product. The vinylene homologs of PhCN form with HCl or HBr in ether imide halides whose color deepens with increasing number of C:C unions and which become increasingly difficultly soluble in ether, a phenomenon which is to be explained by increasing polarity of the C-halogen union. The reduction would then proceed according to the scheme $[\text{RC}^+:\text{NH}][\text{HSnCl}_4]^-$ (V) \rightarrow $\text{RCH:NH} + \text{SnCl}_4$. In 3-fold unsatd. imide halides the halogen acid is split off from the Sn salt because the CN group conjugated with 3 C:C unions cannot hold the halogen acid firmly enough, and reduction, for which formation of the complex V is a prerequisite, cannot occur. A specially constructed apparatus, which made it possible to carry out simultaneously comparative redns. of several nitriles under identical conditions at different temps., is described.